Growth and Characterization of Lanthanum-Doped Yttrium Titanate Single Crystals

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Abstract

Rare earth titanates with composition $RTiO_3$ (where R represents a rare-earth metal) are Mott insulators and key materials in the study of the manifestations of strong electronic correlations, a central subject in modern condensed matter physics. An antiferromagnetic-ferromagnetic transition is observed in the crystals as the radius of the R ion decreases. Yttrium lanthanum titanate single crystals of composition $Y_{1-x}La_xTiO_3$ with x = 0, 0.1, 0.2, and 0.25 were grown in an optical floating zone furnace with growth rates of about 6, 5, 5, and 5 mm/hr, respectively. The quality of the crystals was analyzed using powder x-ray diffraction (XRD), Laue x-ray diffractometry, and a superconducting quantum interference device (SQUID). The magnetic transition temperatures of these samples were found to be 30 K, 17 K, 7 K, and 8 K, respectively.

Introduction

Rare-earth titanates are interesting due to the variety of physical phenomena they exhibit upon doping[1]. They are typical Mott insulators, which are materials that are insulators due to electron-electron interactions not considered in simpler models[2]. These materials are important in the study of spin-orbit coupling, where an electron's orbital motion creates a magnetic moment that interacts with its spin, the inherent magnetic moment of an electron. A particular manifestation of this effect, an antiferromagnetic-ferromagnetic transition, is exhibited in certain rare-earth titanates. This transition appears to occur at a certain value of rare-earth ionic radius. In this transition, the low-temperature arrangement of magnetic moments of the atoms transitions from an alignment in the same direction (ferromagnetism) to an alignment in alternating directions (antiferromagnetism).

In this project, crystals were grown and their Curie temperatures were measured for various dopings of lanthanum in yttrium titanate crystals. The oxygen atmosphere during the growth of the crystals was critical for successful crystal growth. Because Ti^{3+} has a strong tendency to oxidize to Ti^{4+}, any change in the oxygen content could destabilize the crystal formation and produce a pyrochlore of form $R_2Ti_2O_7$. Furthermore, the SQUID measurements were particularly sensitive to oxygen content, so strict oxygen stoichiometry was key to accurate measurements of the magnetic properties of the crystals. Controlling the oxygen stoichiometry was a key challenge in the growth of the crystals. In order to prevent oxidation during the growth, the crystals were grown in a reducing atmosphere. Because residual oxygen was always present in the growth chamber, the stoichiometry of the feed material was altered to $Y_{1-x}La_xTiO_{3-y}$ in order to counteract oxidation. The optimization of the value of y for various x values was a primary result of this project.

Procedure

Rare-earth titanate single crystals were grown using an optical floating zone furnace. The growth chamber was enclosed with a vertical cylindrical quartz tube sealed between two fixed horizontal plates. High output lamps located between these two plates were focused by carefully arranged mirrors on a single point in space inside the growth chamber. Two control rods used to control the movement of growth materials inside the chamber were aligned vertically along the axis of the quartz tube. The atmospheric conditions of the growth chamber were controlled by gas valves that allow high pressures of a controlled gas to build up in the chamber. Typically, the atmosphere of the growth was not varied during a growth, but the power supplied to the lamps and positions of the control rods were carefully managed throughout a growth.

To grow crystals, a feed rod was produced from compressed, stoichiometrically mixed powder, and hung from the top control rod of the floating zone furnace. A seed crystal was fixed to the bottom control rod of the furnace and was aligned such that the feed rod and the seed crystal rotated about the same axis. The growth chamber was then sealed, and 95:5 argon:hydrogen gas was allowed to flow through the chamber in order to evacuate the chamber of atmospheric gases. Then, argon gas continued to flow into the growth chamber until a pressure of approximately 0.5 MPa was achieved. The bottom of the feed rod was melted as it was moved to the focal point of the lamps. The melted portion was then attached to the seed crystal so that a “floating zone” of melted material was attached to the solid seed crystal below and the solid portion of the feed rod above. The two rods were rotated with respect to one another at 20 rpm in order to maintain thermal and compositional homogeneity in the melted zone. The mirrors were then moved vertically with respect to the growth chamber, so that the bottom portion of the melted zone crystallized onto the seed crystal and more of the feed rod was melted. The rate of this movement, known as the growth rate, was a primary factor used to vary growth conditions. As the liquid crystallized on the seed crystal, it preferentially formed a crystal in the same orientation as that of the seed crystal. The seed crystal was ideally a single crystal, in which case the size of the single crystal was increased during this process. When no single crystal seed existed, a polycrystalline seed or a portion of the feed rod was substituted. In these cases, a certain crystal orientation slowly dominated as the growth progressed, transitioning the polycrystalline seed to a single crystal as the growth progressed.

After a growth was completed, the crystal quality was qualitatively determined using Laue x-ray diffractometry. A symmetric pattern with sharp Bragg spots indicated a high quality crystal, while broad Bragg spots indicated a low quality crystal. Furthermore, the magnetic transition temperatures of the crystal was measured using the SQUID. When a ferromagnetic transition occurs, this temperature is known as a Curie temperature, and when an antiferromagnetic transition occurs, the temperature is a Neèl temperature. Larger Curie temperatures for a given crystal composition indicated a higher quality crystal, while lower temperatures indicated an excess of oxygen in the crystal[3]. Powder x-ray diffraction was also used to ensure that the crystal had the desired stoichiometry. As previously noted, the crystal could easily destabilize to $R_2Ti_2O_7$, which has a distinct XRD pattern from $RTiO_3$. The presence of this phase was easily determined with XRD analysis, and indicated a low quality crystal if present.

The primary controllable growth conditions were the lamp power, which controlled the temperature of the growth, and the growth rate. The lamp power was kept close to the melting temperature of the material so that the melt zone did not fall down from between the seed crystal and the feed rod. The growth rate was varied until a successful growth could be easily performed.

Results/Discussion

One result of this process was the determination of the appropriate growth rate for the successful growth of $Y_{1-x}La_xTiO_3$ single crystals with x = 0, 0.1, 0.2, and 0.25. Growth rates of 6 mm/hr for x = 0 and 5 mm/hr were successfully used to produce high quality crystals. As x increased, the compounds were less stable and the production of high quality single crystals was increasingly challenging. Growths of the x = 0.3 compound were attempted at various rates and conditions, but no high quality crystals were produced. Instability at x values between 0.2 and 0.3 has been previously documented[4], so the production of high quality single crystals in this compositional regime was expected to be difficult.

Another important result of the process was the measurement of the magnetic transition temperatures in the high quality crystals. Examples of these transitions can be seen in Figure 1. These values were determined to be 30 K, 17 K, 7 K, and 8 K for x = 0, 0.1, 0.2, and 0.25 respectively. The transition temperature for x = 0 was expected to be approximately 30 K[5], and the present data agreed with this value. The first three transitions were confirmed to be ferromagnetic transitions, while the transition in the x = 0.25 component may have been an antiferromagnetic transition. At x values near 0.25, the $Y_{1-x}La_xTiO_3$ reaches a critical point and a ferromagnetic-antiferromagnetic transition occurs[4].

Conclusion

Appropriate growth conditions for high quality crystal growths of $Y_{1-x}La_xTiO_3$ were determined for x = 0, 0.1, 0.2, and 0.25. High quality crystals could be produced with growth rates of about 5 mm/hr in a 0.5 MPa 95:5 argon:hydrogen atmosphere. The Curie temperature for the high quality samples was 30 K for $x = 0$, 17 K for $x = 0.1$, and 7 K for $x = 0.2$. A magnetic transition that may have been ferromagnetic or antiferromagnetic occurred at 8 K for $x = 0.25$.

The samples produced by these methods have been and will continue to be further analyzed with transport measurements, neutron scattering, and other analysis techniques outside the scope of this report. Similar methods will be applied in the effort to continue to grow high quality crystals with x values that range fully from 0 to 1, with special focus on x values near the transition at $x \approx 0.3$.

References

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Figures

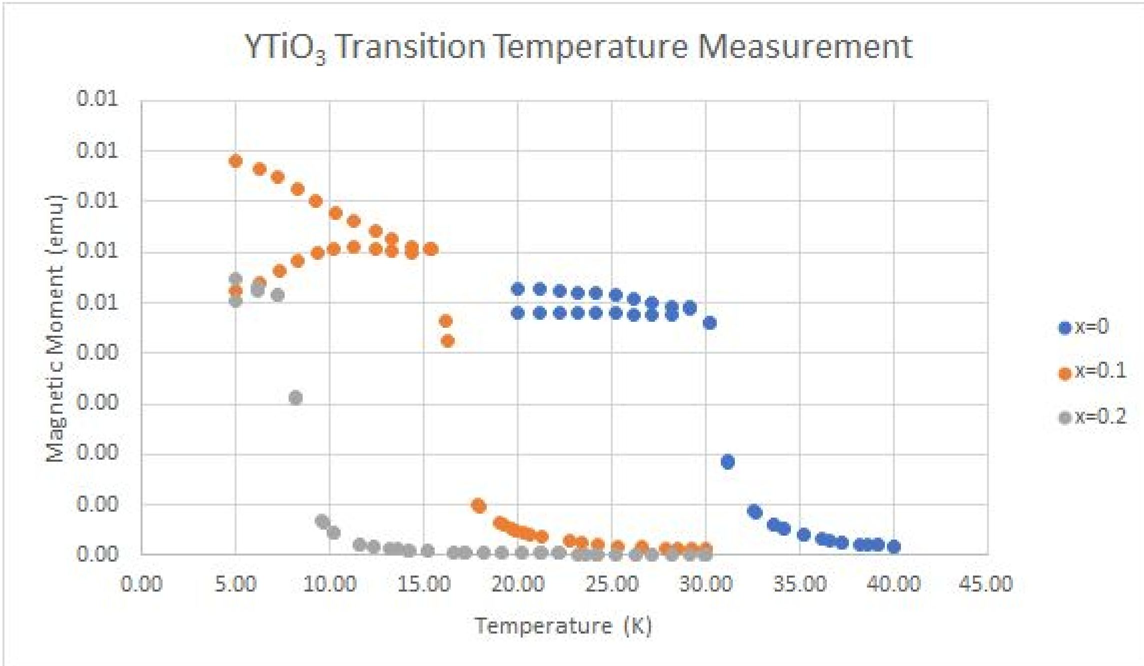

Figure 1: Field cooled magnetization as a function of temperature for x = 0, 0.1, and 0.2 in a magnetic field of 50 Oe. Data for x = 0.2 is scaled by a factor of 0.1.